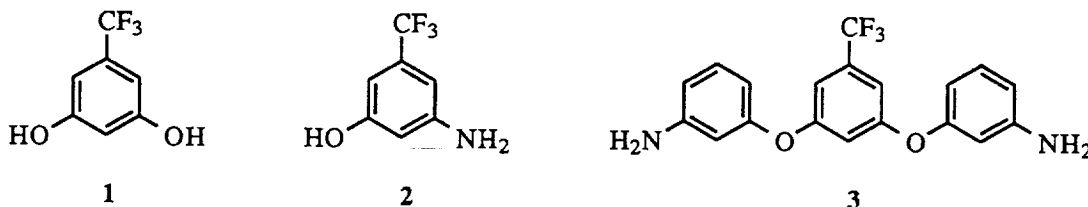


## NEW MONOMERS FOR HIGH PERFORMANCE POLYMERS

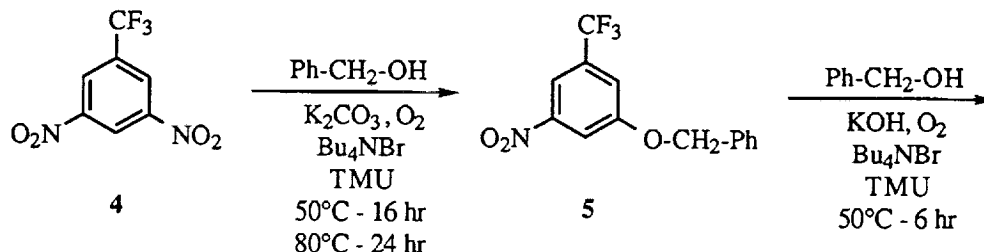
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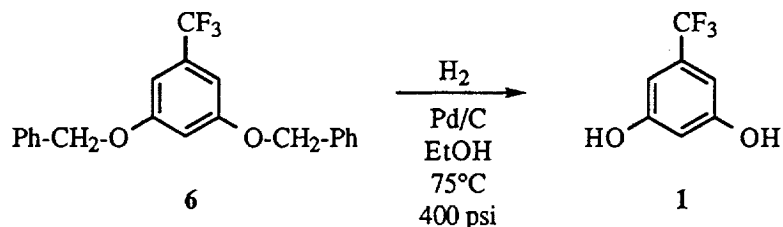
This laboratory has been concerned with the development of new polymeric materials with high thermo-oxidative stability for use in the aerospace and electronics industries. Currently, there is special emphasis on developing matrix resins and composites for the high speed civil transport (HSCT) program. This application requires polymers that have service lifetimes of 60,000 hr at 350°F (177°C) and that are readily processible into void-free composites, preferably by melt-flow or powder techniques that avoid the use of high boiling solvents. Recent work has focussed on copolymers which have thermally stable imide groups separated by flexible arylene ether linkages (1,2), some with trifluoromethyl groups attached to the aromatic rings (3). The presence of trifluoromethyl groups in monomers and polymers often improves their solubility and processibility.

The goal of this research was to synthesize several new monomers containing pendant trifluoromethyl groups and to incorporate these monomers into new imide/arylene ether copolymers. Initially, work was begun on the synthesis of three target compounds. The first two, 3,5-dihydroxybenzotrifluoride, **1**, and 3-amino-5-hydroxybenzotrifluoride, **2**, are intermediates in the synthesis of more complex monomers. The third, 3,5-bis[3-amino-phenoxy]benzotrifluoride, **3**, is an interesting diamine that could be incorporated into a polyimide directly.

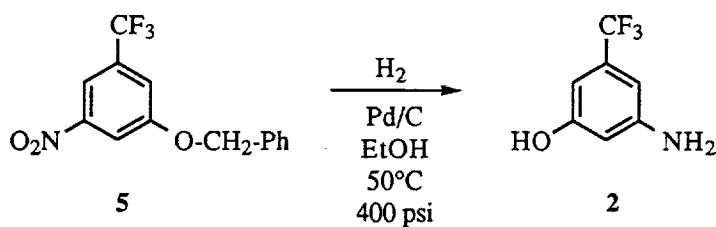


Two syntheses of 3,5-dihydroxybenzotrifluoride, **1**, are reported in the literature (4,5) beginning with commercially available 3,5-dinitrobenzotrifluoride, **4**. Both involve four steps, including reactions that tend to give low yields of the desired products. Based on a literature procedure (6), a new synthetic route to **1** has been devised involving stepwise replacement of the nitro groups of **4** with benzoxy groups to give the benzyl ethers, **5** and **6**. The solvent for the reaction is tetramethylurea (TMU). Hydrogenolysis of **6** to give **1** completes the convenient three step synthesis.





Two methods for preparing 3-amino-5-hydroxybenzotrifluoride, **2**, from 3,5-dinitrobenzotrifluoride, **4**, have also been reported in the literature (4,7). Both methods involve three steps, including low yield reactions. By taking advantage of the fact that the benzyl ether of 3-benzyloxy-5-nitrobenzotrifluoride, **5**, is cleaved at the same time the nitro group of **5** is being reduced by catalytic hydrogenation, a straightforward two step synthesis of **2** was accomplished.



An attempt to prepare 3,5-bis[3-aminophenoxy]benzotrifluoride, **3**, in one step by substitution of both nitro groups of 3,5-dinitrobenzotrifluoride, **4**, with the sodium salt of 3-aminophenol using the general procedure of reference (3) was unsuccessful. A two step procedure similar to that used to make 3,5-dibenzyloxybenzotrifluoride, **6**, may produce the desired product and should be tried.

Future work in this area should include scaling up the syntheses of **1** and **2** and investigating the substitution of more common solvents for TMU. Standard techniques (1,2,3) could then be used to incorporate these structures into diamine and dianhydride monomers for the preparation of new polyimides.

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